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Solid State Synthesis, Characterization and Antimicrobial Study of 4,4′-Bipyridinecopper (II) Complexes

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ABSTRACT

The state of the art in crystal engineering and mechanochemistry were exploited to synthesize 4,4′-bipyridine copper (II) chloride and 4,4′-bipyridine copper (II) (*MOF*) by mechanochemical grinding of [4,4′-H_2bipy]Cl_2 with copper(II) acetate and the subsequent grinding of the coordination compound [$CuCl_2$4,4′-bipy] with an external base (K_2CO_3). The complexes obtained were characterized by elemental analysis, infrared spectral studies, decomposition temperature determination, conductivity measurement and solubility test. The molar conductivity value range from 38.0-40.2 $\Omega^{-1}cm^2\ mol^{-1}$, and its decomposition temperature ranges from 171–189^oC. The elemental analytical data and infrared values indicated that the complexation has taken place. The complexes were effective against some selected bacteria and fungi (*escherichia coli*, *pseudomonas aeruginosa*, *streptococcus pneumonae*, *staphylococcus aureus*, *klebsiella specie* and *penicillium specie*, *meterhizium specie*, *aspergilus species*) at 1000µg/disk (highest concentration).

Keywords: 4,4′-bipyridinium chloride, mechanochemistry, metal-organic framework

INTRODUCTION

Development of new materials for solid state science and technology depends on access to new synthetic methods; hence the need for the exploration of new frontiers in the science of synthesis without the use of solvents. Recently a number of researchers have shown that a range of coordination compounds can be prepared without recourse to solution methods (James *et al*., 2012)

Over the past few decades, much attention has been devoted to the search of novel materials based on metal-organic frameworks (MOFs), motivated by their intriguing structures, new topologies, and potential applications. Since the onset, 4,4'-bipyridine (bipy) has been widely used to construct supramolecular architectures, for it has two potential binding sites which are arranged in a divergent (*exo*) fashion and has a rigid structure which will help in the predictability of network geometries (Lusi, 2008).

The different isomers of bipyridine have been intensively studied as ligands because of their stability and robustness. They give different structural types, acting either in a chelating or bridging manner, depending on the location of the nitrogen atoms, and have been found useful in a number of applications. Chelating 2,2′-bipyridine, for example, forms molecular materials used in dyes for solar cells or in Application Programming Interfaces (APIs). Conversely the 4,4′ isomer (and its analogues), typically acts as a bridge between two metal centers, and has been successfully used to form mono-or multi-dimensional networks (Lusi, 2008).

Development of new materials for solid state science and technology depends on access to new synthetic methods; hence the need for the exploration of new frontiers in the science of synthesis without recourse to the use of solvents. In recent years solid-state synthesis has possibly gained more attraction because these reactions are sometimes more convenient than using solvent-based synthesis, cost effective, and can reduce environmental contamination. In addition, safety may be increased and work-up is considerably simplified, and more importantly solid-state methods can provide much faster access to complexes which are inaccessible or usually take a long time to synthesize from solution or other methods (Kurawa, 2008). For example, the assembly of a hexa-palladium bowl-shaped cluster gave 90% yield at room temperature by simply grinding [$Pd(NO_3)_2$en] and a tripodal ligand (2,4,6-(tripyridyl)-1,3,5-triazine), was achieved in only ten minutes while a similar reaction with in aqueous solution at 70 ºC took 4 hours to reach 56% completion. (Orita *et al*., 2002).

Solid state synthesis of [$CuCl_4$][4,4′-H_2bipy] and [$CuCl_2$4,4′-bipy] was reported when $CuCl_2.5H_2O$ was ground with [(4,4′-H_2bipy)Cl_2] and $CuCO_3$ with [(4,4′-H_2bipy)Cl_2] respectively (Lusi, 2008). Solid-state reactions are usually achieved *via* solid-solid or solid-gas reactions, and in most cases involve bringing two reactants together to form a product without using bulk solvent. This is usually achieved when the solid reagents are ground together or exposed to gaseous substances. The processes are believed to be conceptually related but have distinct mechanistic approaches (Braga *et al.*, 2007).

This paper is concerned with the design and synthesis of crystalline solids which are planned to offer chemical reactivity towards dehydrochlorination to yield coordination compounds with novel properties. It is aimed at the exploitation of state of the art techniques in crystal engineering solid state chemistry to prepare coordination polymers and metal-organic frameworks and explore their possible application in anti-microbial studies.

MATERIALS AND METHODS

All the reagents used were of analar grade and were used without further purification. Glasswares were washed and dried before the start of any experiment. All the complexes were synthesized by grinding with pestle and motor characterized using FTIR-8400S Fourier Transform Infrared Spectrophotometer, Elemental analysis of the complexes was carried out using Flash 2000 organic elemental analyzer, at Ahmadu Bello University, Zaria, molar conductance was studied using Jenway conductivity meter model 4000 and decomposition temperature were obtained using a Gallenkemp melting apparatus.

Preparation of the Ligand:

5g of 4,4'-bipy was put in a 50ml beaker, the beaker and the content were immersed in a 1000ml beaker containing 100ml concentrated hydrochloric acid in an erected position, the 1000ml beaker was covered so as to allow the escaping HCl gas to enter the 50ml beaker directly. This was allowed to stand for 6hrs to yield [(4,4′-H_2bipy)]Cl_2 Adams, *et al.*, 2010. This product was confirmed by Infrared spectrum and Elemental analytical data.

Synthesis of [{$CuCl_2$(4,4′-bipy)}$_n$]

0.229g (1mole) of [4,4′-H_2bipy]Cl_2 and 0.199g (1mole) of $Cu(CH_3COO)_2.H_2O$ were ground in an agate mortar for 2mins. A mixture of Blue-green and white colours turn to turquoise blue with a release of very strong odour of acetic acid was obtained.

Synthesis of [{Cu(4,4′-bipy)}$_n$]

0.03g (0.1mole) of [{$CuCl_2$(4,4′-bipy)}$_n$] was ground with 0.014g (0.1mole) of K_2CO_3 for 2mins. A dried sky blue powder was obtained.

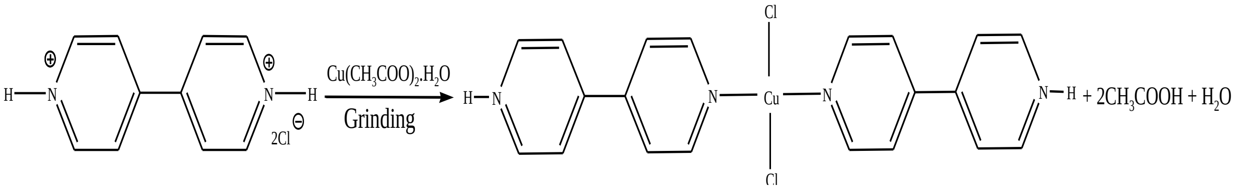
RESULTS AND DISCUSSION:

The infrared Spectrum of the protonated ligand showed a peak at 3429cm^{-1} and 3027cm^{-1} which are assigned to N-H and H-Cl bonds respectively, these peaks revealed that the original 4,4′-bipyridine was protonated when compared with the Infrared spectrum of the original 4,4′-bipyridine.

4,4′-bipyridinedichlorocopper (II) [{$CuCl_2$(4,4′-bipy)}$_n$]

Grinding of copper (II) acetate with 4,4′-bipyridinium chloride resulted in the formation of the above product. The infrared spectrum shown the presence of Cu-Cl and Cu-N bonds at 485cm^{-1} and 562cm^{-1} respectively (Table 1). The elemental analytical data revealed the percentage of nitrogen, carbon and hydrogen found to be 8.97%, 42.08% and 1.88% respectively, while the calculated percentage using chemputer is 9.64%, 41.33% and 2.77% for nitrogen, carbon and hydrogen (Table 2).

The result of the molar conductivity measurement (Table 3) was found to be 38.0 Ω^{-1}cm^{2} mole^{-1} and the electrical conductivity was 38.0 x 10^{-6} Ω^{-1}cm^{-1}, the lower values obtain showed that the complex is non-elctrolyte (Sekhon, *et al.*, 2010). The decomposition temperature was found to be 189^{o}C, is higher than the reactants copper (II) acetate (≥115^{o}C) and protonated 4,4′-bipyridinium chloride (≥112^{o}C), the decomposition temperature of the complex is higher and this is due to the formation of copper chlorine and copper nitrogen bonds (Table 3). The solubility test (Table 4) revealed that the complex is soluble in water, hydrogen peroxide and concentrated hydrochloric acid and slightly soluble in ethanol and acetic acid. The compound has shown better activity at highest concentration (1000 µg/disk) in all bacteria (Table 5), and also in the fungi with the exception of *Meterhizium specie* where it showed no activity (Table 6).



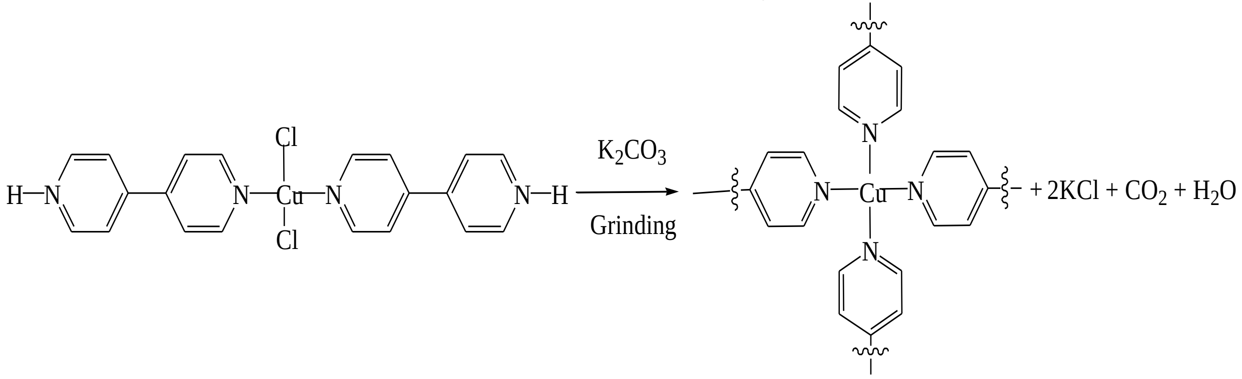
Equation 1: Formation of [{$CuCl_2$(4,4′-bipy)}$_n$]

While grinding, a strong odour of acetic acid was perceived, which may be attributable to the mechanochemical breakage of Cu-O bonds in the copper (II) acetate and the N-H bond in the 4,4′-bipyridinium chloride salts respectively, the complete breakage of the above bonds lead to the formation of Cu-Cl and Cu-N bonds and resulted in the formation of 4,4′-bipyridinedichlorocopper (II) and the libration of acetic acid (equation 1). A mixture of green and white color turns to turquoise. The same result was obtained when copper (II) carbonate was ground with 4,4′-bipyridinium chloride.

4,4′-bipyridinecopper (II) [{Cu(4,4′-bipy)}$_n$]

Mechanochemical grinding of [{CuCl$_2$(4,4′-bipy)}$_n$] with potasium carbonate in the ratio 1:1 yields 4,4′-bipyridinecopper (II). This resulted in the formation of metal-organic frameworks (*MOFs*) which was achieved by the abstraction of the two chloride ions by potassium ions and the deprotonation of the nitrogen atoms of the 4,4’ bipy molecules. In the process Cu-Cl bonds are severed leading to the formation of Cu-N bonds and KCl and H_2O are produced as by-products (equation 2). Similar reactions are reported imidazole and pyrazole ligands by Adams *et al.* (2010). The elemental analysis is found to be 5.98%, 32.28% and 2.24% in respect of nitrogen, carbon and hydrogen while the calculated percentage elemental analytical data of nitrogen, carbon and hydrogen is 7.60%, 32.56% and 2.18% respectively.

The molar conductivity measurement was found to be 40.2 $\Omega^{-1}cm^2$ mole^{-1} and the electrical conductivity was 40.2 x 10^{-6} $\Omega^{-1}cm^{-1}$, these low values revealed that there is no free ion out of the coordination sphere and the complex is non-electrolyte. The decomposition temperature is 171^{o}C, comparing with melting temperature of copper (II) acetate (≥115^{o}C) and that of protonated 4,4′-bipyridinium chloride (≥112^{o}C), [{CuCl$_2$(4,4′-bipy)}$_n$] have shown higher decomposition temperature which is as a result of its stability.



Equation 2: Formation of [Cu(4,4′-bipy)$_n$]

The solubility test have revealed that: the complex is soluble in hydrogen peroxide and concentrated hydrochloric acid and slightly soluble in water, ethanol and acetic acid, this is because covalent complexes are expected to be soluble in covalent solvents (like dissolves like) (Table 3). The complex have shown activity on *Psuedomona aeruginosa* bacteria at highest concentration and showed activity at highest concentration on all fungi. A mixture of turquoise blue and white turn to dried sky blue powder.

Table 1: IR Spectral Analysis of the Metal (II) Complexes

FITR Value/ Samples	***v*(M-Cl) cm^{-1}**	***v*(M-N) cm^{-1}**	***v*(C-H) cm^{-1}**	***v*(C=N) cm^{-1}**	***v*(C-C) cm^{-1}**
[{CuCl$_2$(4,4′-bipy)}$_n$]	485	562	1347	1469	1207
[Cu(4,4′-bipy)$_n$]		569	1408	1408	1217

Keys: ***v*** **=** Wave number; **M =** Metal

Table 2: Elemental Analytical Data of the Metal (II) Complexes

		Percentage (%)		
Complexes	**Elements**	**Nitrogen**	**Carbon**	**Hydrogen**
$[\{\mathrm{CuCl_2}(4,4'\text{-bipy})\}_n]$	Calculated	9.64	41.33	2.77
	Found	8.97	42.08	1.88
$[\mathrm{Cu}(4,4'\text{-bipy})_n]$	Calculated	7.60	32.56	2.18
	Found	5.98	32.28	2.24

Table 3: Decomposition Temperature, Molar and the Electrical conductivity

Complexes	**Docomposition Temp. (^{o}C)**	**Electrical conductivity (Ω^{-1}cm^{-1})**	**Molar Conductivity (Ω^{-1}cm^{2} mole^{-1})**
$[\{\mathrm{CuCl_2}(4,4'\text{-bipy})\}_n]$	189	38.0×10^{-6}	38.0
$[\mathrm{Cu}(4,4'\text{-bipy})_n]$	171	40.2×10^{-6}	40.2

Table 4: Solubility Test Results

Solvents/ Complexes	**Water**	**Ethanol**	**Hydrogen Peroxide**	**Acetic Acid**	**Conc. HCl**
$[\{\mathrm{CuCl_2}(4,4'\text{-bipy})\}_n]$	S	SS	S	SS	S
$[\mathrm{Cu}(4,4'\text{-bipy})_n]$	SS	SS	S	SS	S

Key: S = Soluble; SS = Slightly Soluble

Table 5: Anti-Bacterial Activity Inhibition Zones

Complexes	Concentrations (µg/disk)	*E. coli* (mm)	*Ps.* (mm)	*Strep.* (mm)	*Staph.* (mm)	*Kleb.* (mm)
$[\{\mathrm{CuCl_2}(4,4'\text{-bipy})\}_n]$	50	6	6	11	11	6
	500	13	6	13	20	13
	1000	20	13	17	23	18
$[\mathrm{Cu}(4,4'\text{-bipy})_n]$	50	6	6	6	6	6
	500	6	18	6	6	6
	1000	6	38	6	6	6
CONTROL (Gentemecyn)	10	45	31	38	37	46

Key: *E. coli = Escherichia Coli*
Ps = Psuedomona aeruginosa
Strep = Streptococcus pneumonae
Stap = Staphylococcus aureus
Kleb = Klebsiella Specie

Table 6: Anti-fungal Activity Inhibition Zones

Complexes	Concentrations (µg/disk)	*Pen* (mm)	*Met* (mm)	*Asp* (mm)
[{$CuCl_2$(4,4′-bipy)}$_n$]	50	6	6	6
	500	13	6	10
	1000	26	6	15
[Cu(4,4′-bipy)$_n$]	50	6	6	6
	500	6	6	6
	1000	13	13	10
CONTROL (Apron plus)	10	38	28	20

Key:
Pen = Penicillium Specie
Met = Meterhizium Specie
Asp = Aspergilus Specie

CONCLUSION

In conclusion we note that

1. Basic metal salts such as $Cu(CH_3COO)_2.H_2O$ can be used as a metal source to synthesize polymeric metal (II) complexes like ([{$CuCl_2$(4,4′-bipy)}$_n$]).
2. Metal organic frameworks (MOFs) ([Cu(4,4′-bipy)$_n$]) can be synthesized in a one-step solid state method.
3. Deprotonation reaction can be carried out in solid state with bases like K_2CO_3 which are

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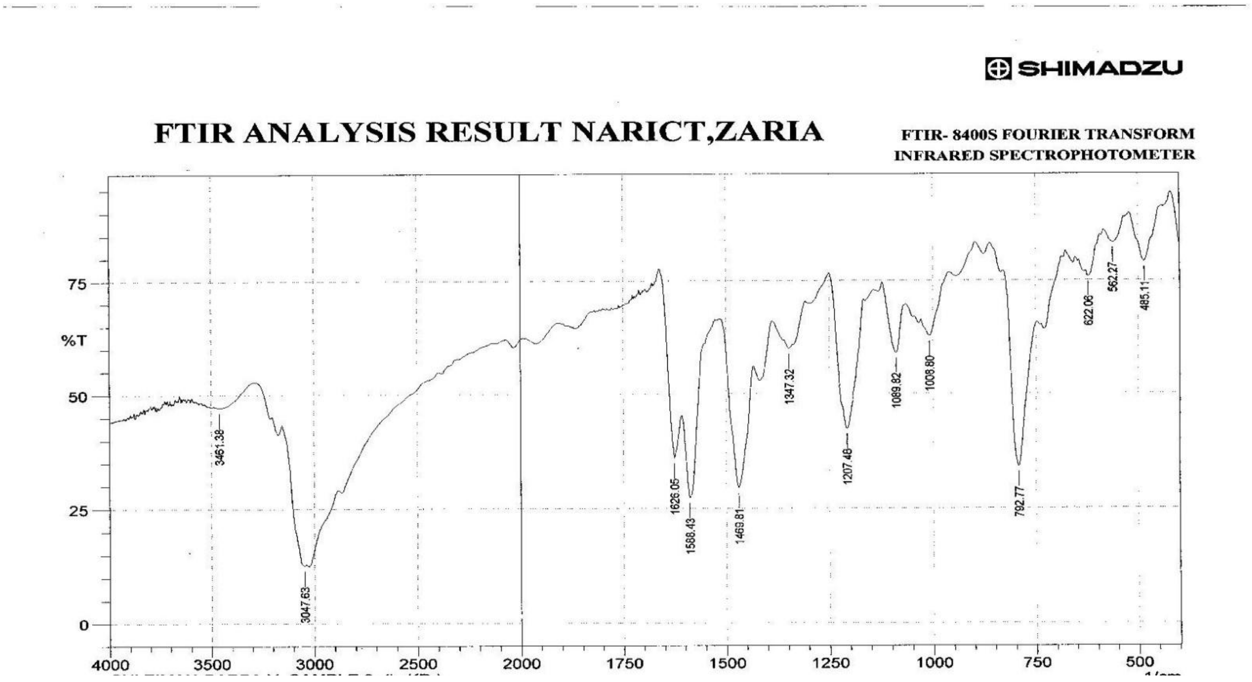
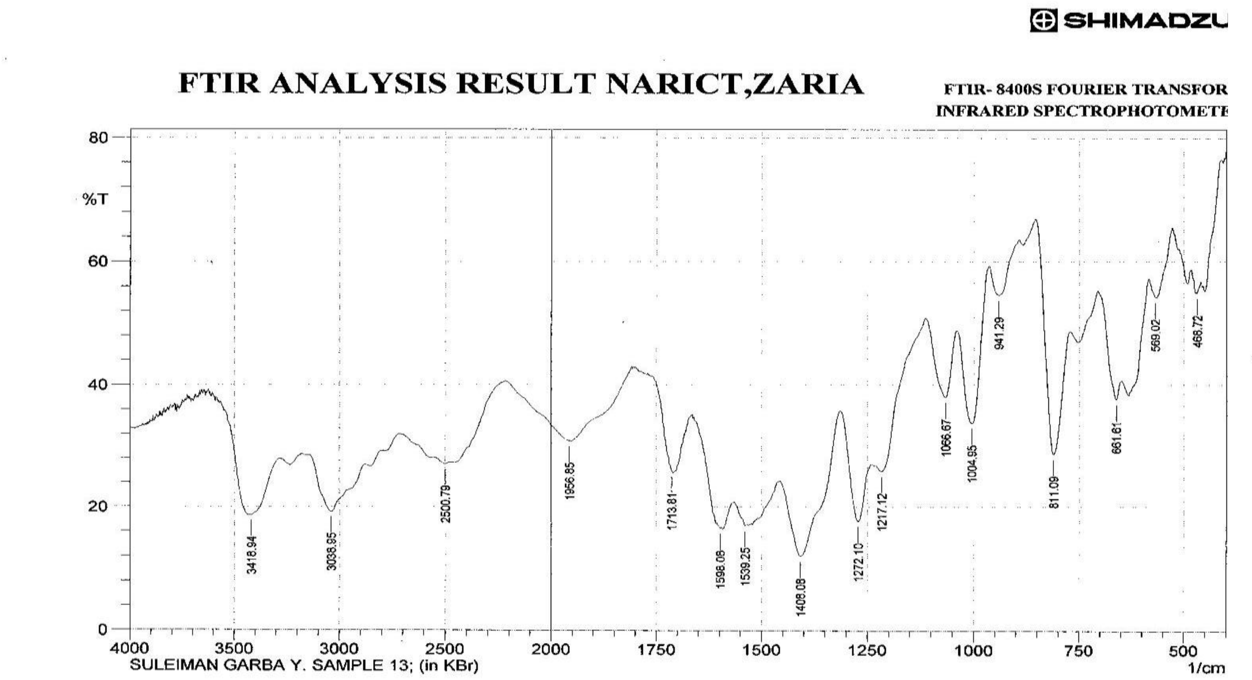
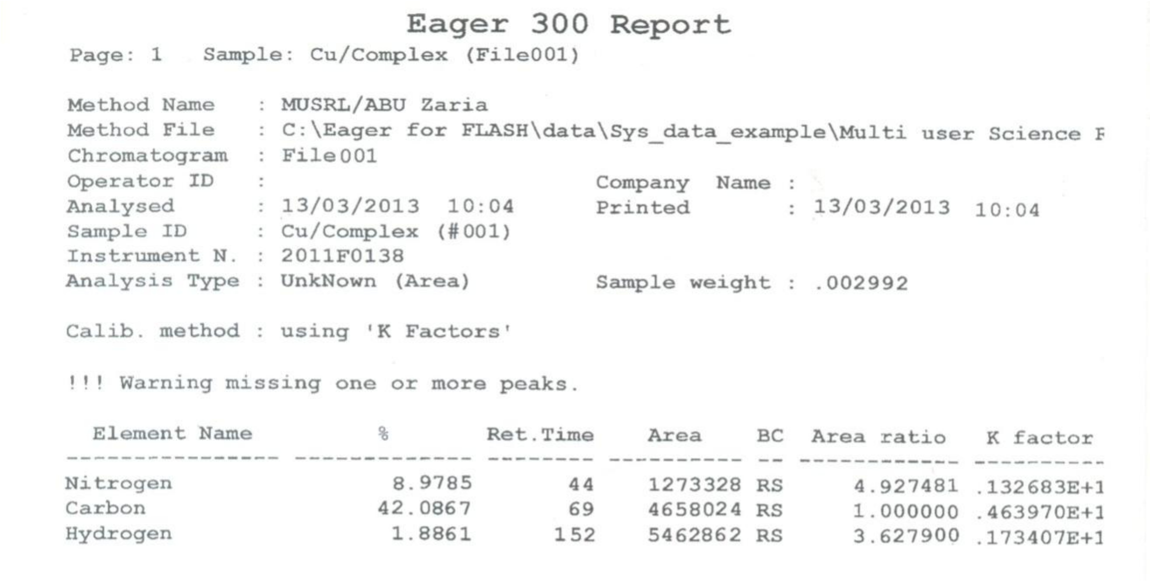
Appendix 1: Infrared Spectrum of 4,4′-bipyridinedichlorocopper (II)



Appendix 2: Infrared Spectrum of 4,4′-bipyridine copper (II)



Appendix 3: Elemental analysis result of 4,4′-bipyridinedichlorocopper (II)



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                         Eager 300 Report
Page: 1   Sample: Cu/Complex (File001)

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Method File    : C:\Eager for FLASH\data\Sys_data_example\Multi user Science F
Chromatogram   : File001
Operator ID    :                         Company  Name :
Analysed       : 13/03/2013  10:04       Printed        : 13/03/2013  10:04
Sample ID      : Cu/Complex (#001)
Instrument N.  : 2011F0138
Analysis Type  : UnkNown (Area)          Sample weight : .002992

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

  Element Name            %        Ret.Time     Area     BC  Area ratio   K factor
---------------- ------------- -------- ---------- -- ------------ ----------
Nitrogen                8.9785        44    1273328 RS     4.927481 .132683E+1
Carbon                 42.0867        69    4658024 RS     1.000000 .463970E+1
Hydrogen                1.8861       152    5462862 RS     3.627900 .173407E+1
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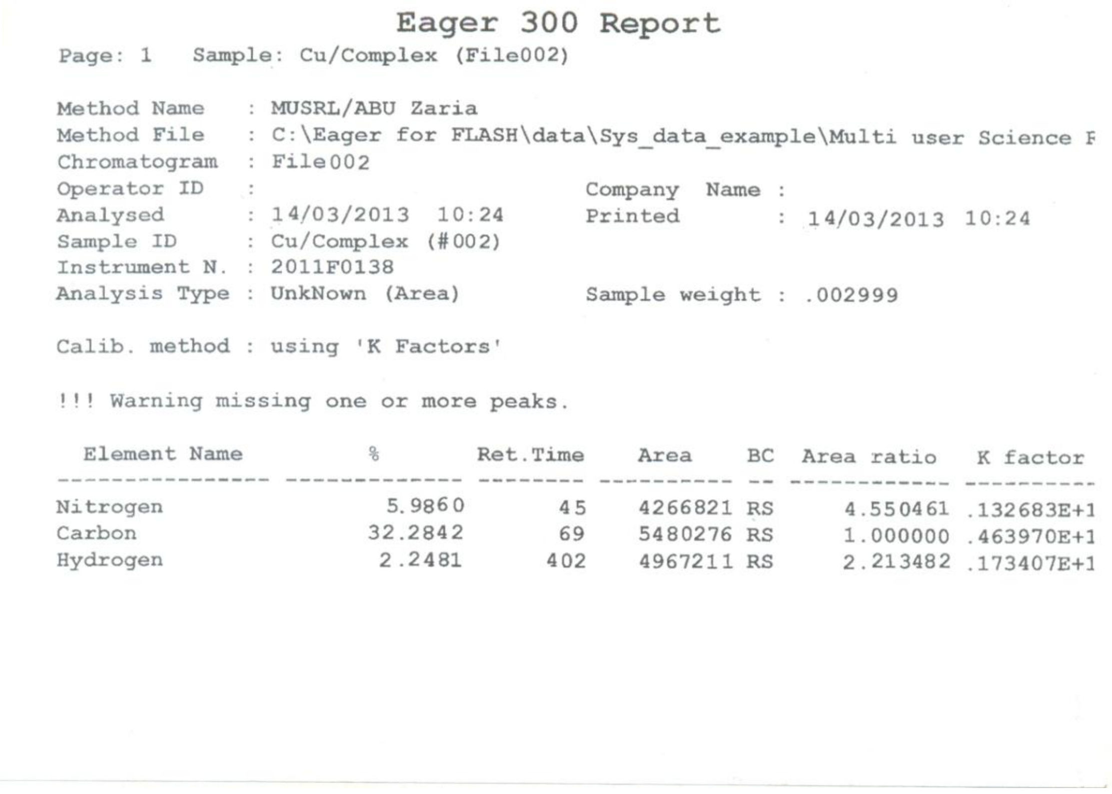
Appendix 4: Elemental analysis result of 4,4′-bipyridine copper (II)



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                         Eager 300 Report
Page: 1   Sample: Cu/Complex (File002)

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Chromatogram   : File002
Operator ID    :                         Company  Name :
Analysed       : 14/03/2013  10:24       Printed        : 14/03/2013  10:24
Sample ID      : Cu/Complex (#002)
Instrument N.  : 2011F0138
Analysis Type  : UnkNown (Area)          Sample weight : .002999

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

  Element Name            %        Ret.Time     Area     BC  Area ratio   K factor
---------------- ------------- -------- ---------- -- ------------ ----------
Nitrogen                5.9860        45    4266821 RS     4.550461 .132683E+1
Carbon                 32.2842        69    5480276 RS     1.000000 .463970E+1
Hydrogen                2.2481       402    4967211 RS     2.213482 .173407E+1
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